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A1

WO 02/076888

(54) Title: METHOD FOR THE PREPARATION OF STABLE SUSPENSIONS AND POWDERS OF SINGLE CARBON NANOTUBES

(57) Abstract: A method is provided for exfoliation of carbon nanotubes and for the preparation of a stable aqueous suspension thereof containing dispersed, essentially single tubes, using a water-soluble polymeric material. A powder of carbon nanotubes is further provided, that can be re-dispersed to form a stable suspension. Said nanotubes can be used in electronics, printing, coatings, thin layers, molecular machines, and for the production of composite materials.

METHOD FOR THE PREPARATION OF STABLE SUSPENSIONS AND POWDERS OF SINGLE CARBON NANOTUBES

Field of the Invention

The present invention relates to the exfoliation of carbon nanotubes and to a method for the preparation of a stable aqueous suspension thereof. The 5 invention also provides for a powder of carbon nanotubes that can be re-dispersed to form a stable suspension. The invention further relates to the use of the carbon nanotubes in electronics, printing, coatings, thin layers, molecular machines, and production of composite materials.

Background of the Invention

Carbon nanotubes, either in form of Single Wall Nanotubes (SWNT) or in form of Multi Wall Nanotubes (MWNT), are macromolecular threads with a typical diameter of few nanometers and a length of up to tens of microns. The single tubes exhibit superior mechanical and electrical properties, 15 Young modulus reaching 1 TPa (M.S. Dresselhaus et al., Science of Fullerenes and Carbon Nanotubes, Academic Press, New-York, 1996), and current density 10^9 Acm^{-2} , as well as excellent thermal stability (W. A. de-Haar et al., Science 281 (1998) 1744).

20 Nanotubes tend to cluster; however, their most desired form is well separated tubes, of either SWNT or MWNT. Carbon nanotubes are currently at the focus of theoretical and experimental research (S.J. Tans et.al, Nature 386 (1997) 474; E.W. Wong et al., Science 277 (1997) 1971).

25 The superb mechanical properties of carbon nanotubes raise high expectations regarding their utilization as reinforcing fillers in polymeric matrices, forming lightweight super strong meso-composites. In order to

fulfill these expectations, good mechanical coupling and in particular, stress transfer between the polymeric matrix and the nanotubes are sought for.

- 5 A second discipline in which carbon nanotubes and particularly SWNT hold a promise, is molecular electronics. Here SWNT may fulfill two different roles: They may serve as active components in nano-sized devices such as field-effect transistors and electron emission sources. Alternatively, they may serve as molecular wires, connecting various
10 nano-components.

However, discrepancies are often found between theoretical predictions and experimentally observed properties of carbon nanotubes as they are prepared. The reason is a tendency of carbon nanotubes to crystallize in
15 ropes which are entangled into networks. Van-der-Waals interactions between two tubes lead to their alignment, and to their consequent packing into crystalline ropes which may contain 100 to 500 tubes (J. Liu et al., Science 280 (1998) 1253). The crystalline nature of the ropes gives rise to a characteristic X-ray scattering pattern. The different levels of
20 aggregation of carbon nanotubes were found to affect both their electrical and mechanical behavior (S. Sanvito et al., Phys. Rev. Lett. 84 (2000) 9). Aggregated ropes are fragile, and even when well aligned, do not exhibit the expected electrical properties, such as field-emission intensity.

- 25 Current studies focus on manipulation and orientation of the tubes (P. J. de Pablo et al., Advanced Materials (2000) 573). One of the novel approaches is based on the synthesis of dense, ordered arrays of carbon nanotubes on a solid substrate. In some of the reported studies, each entity is a rope rather than a single tube. The aligned ropes exhibit
30 inferior properties in comparison to those expected from well-separated tubes. There is also need of a surface treatment that would lead to better adhesion at the interface between matrix and carbon tubes.

Recently an approach for post-synthesis alignment of carbon nanotubes was described by Vigolo et al. (B. Vigolo et.al, Science 290 (2000) 1331). In this method, as-produced SWNT are dispersed in low concentrations, up to 0.85 weight %, in aqueous solutions of an ionic surfactant, sodium dodecylsulfate (SDS). The dispersed ropes are then re-condensed in a shear flow into fibers and ribbons of well aligned ropes.

There is a need for new methods for the interfacial engineering of carbon nanotubes. Efforts for developing a simple method for the dispersion of nanotube networks into single ropes, and ropes into separate tubes, have not been successful. It is therefore an object of the present invention to provide a method for the preparation of stable aqueous dispersions of well separated single carbon nanotubes. Another purpose of the invention is to provide a dry form of well separated carbon nanotubes, easy for storage and manipulation, and ready for use in various fields of applications and technologies, including electronics, and material engineering. It is still another object of the invention to provide an adhesive interface between the carbon tubes and a polymeric matrix where the tubes serve as reinforcing agents for the matrix.

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Summary of the Invention

The present invention relates to the exfoliation of carbon nanotubes and to a method for the preparation of a stable aqueous suspension thereof, comprising adding to an aqueous medium, prior to the addition of carbon nanotubes or thereafter, a water-soluble polymeric material, thereby to separate the nanotubes into dispersed, essentially single tubes. The polymer adsorbs on the carbon tubes, interferes with strong forces between them, prevents their aggregation, and enables the formation of suspensions of polymer-coated carbon nanotubes that are stable, and can be as concentrated as 65 weight percents or more. The polymer-coated tubes may serve as adhesion promoters leading to the formation of highly

adhesive interfaces between the tubes and a polymeric matrix. A preferred polymer for preparation of the suspensions is a water soluble polymer, either synthetic or natural one, wherein the mass ratio of polymer to carbon nanotubes ranges preferably from 0.05 to 20.

5

The invention also provides for a powdered form of single, well separated carbon nanotubes that can be easily re-dispersed to form a stable suspension. The dry form is simple to handle, and enables one to prepare suspensions of desired volumes and concentrations of the well-separated non-aggregated tubes quickly and easily. This form of nanotubes is convenient for storing, manipulating, and immediate use. The invention further relates to the use of the polymer-coated single carbon nanotubes in electronics, printing, coatings, thin layers, molecular machines, and production of composite materials.

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Brief Description of the Drawings

The above and other characteristics and advantages of the invention will be better understood through the following illustrative examples, and with reference to the appended drawings, wherein:

20 Fig. 1 Shows wide angle x-ray spectra of (a) rope structure of a two-dimensional triangular lattice of as-produced carbon nanotubes, and (b) the wide angle x-ray spectra of a dried powder prepared from a solution with a ratio of 15 wt % gum arabic (GA) to 3 wt% SWNT. Inset shows the reflections of the Co/Ni catalyst used in the synthesis of carbon nanotubes;

25 Fig. 2 Is a SEM micrograph of Au spattered as-received nanotube powder, the arrow indicating a single rope;

Fig. 3 Shows the appearance of 0.05 % (weight percent) SWNT dispersions in different aqueous solutions after 2 months: (A) 2% GA, (B) 5 % GA, (C) 5 % SDS, (D) 15 % SDS, (E) 5 % CTAC, (F) 15 % CTAC;

30 Fig. 4 Is a cryo-TEM micrograph obtained from a dispersion of SWNT. The dispersion was prepared by re-dispersing a dried powder of GA coated

carbon nanotubes in pure water. The powder was prepared by drying an aqueous solution of 15 % GA and 3 % SWNT. The arrows indicate flexible SWNT (S), the Co/Ni catalyst (C), radiation damage of the lacey support (D), and a Multiwall Nanotube (M); and

5 Fig. 5 shows FTIR spectra of (a) pure GA, and (b) dry SWNT prepared according to Example 2. The samples were prepared by mixing the relevant material with KBr in a ratio of 5:100.

Detailed Description of the Invention

10 We discovered that some polymeric compounds enable the preparation of stable aqueous suspensions of single carbon nanotubes. Without committing ourselves to any particular theory, based on our experimental findings (presented in the figures), we suggest that polymers, preferably hydrophilic polymers, adsorb to the carbon tubes and induce an inter-tube repulsion. This prevents their aggregation, and enables the exfoliation of 15 the carbon nanotubes, and the formation of a suspension comprising well separated, polymer-coated single tubes.

20 A water-soluble polymer and a powder of as-produced nanotubes, containing bundled arrays of ropes, are mixed in any order with water or an aqueous solution. The mixture is then sonicated or mixed by a mixer, and a black, ink-like suspension, is obtained. This suspension, containing separated, polymer-coated tubes, is ready for the intended use. Said suspension is stable for months.

25 Surprisingly, we found that the above obtained suspension can be dried by known methods, and the powder which is obtained can be easily re-dispersed in pure water or in water solutions to a required concentration of up to 65 weight % (or more) of polymer-coated carbon tubes, wherein 30 shaking, mixing, or sonication can be used for said re-dispersal. The resulting suspension is also stable for months. Said drying, and the

removal of water from the suspension of carbon nanotubes, may comprise evaporation, lyophilization, centrifugation, and filtration.

- The polymer used in this invention is preferably a hydrophilic polymer,
5 still more preferably a charged polymer, either of natural or synthetic origin, and the mass ratio of said polymer to carbon nanotubes ranges from 0.05 to 20. Said polymer is chosen from polysaccharides and polypeptides. Said polymer can be a water soluble synthetic polymer.
- 10 In preferred embodiments of this invention, the polymer comprises gum arabic, carrageenan, pectin, polygalacturonic acid, alginic acid, chitosan, and derivatives thereof.
- In a preferred embodiment, gum arabic (GA) is dissolved in deionized
15 water to a concentration of 15%, and as-produced carbon tubes are admixed to a concentration of 3%, followed by sonication at room temperature, the time of sonication being preferably from 5 to 20 minutes.
- 20 It has also been found by us (Fig.3) and others (B. Vigolo et.al, Science 290 (2000) 1331) that other surfactants, do not cause the separation of ropes into single tubes, and exhibit a minor or no dispersing effect on the clustered ropes, confirming the negative results of the prior art, mentioned above. Other types of surfactants, at various concentrations have been
25 checked, for example SDS, cetyltrimethyl ammoniumchloride (CTAC), dodecyltrimethylammonium bromide (DTAB), pentaethoxylethyleneether (C₁₂E₅), dextrin and polyethyleneoxide (MW about 300,000). None of the materials acted as an efficient dispersing agent for nanotubes in aqueous solutions, and even the best of them could
30 not even stabilize 0.35% (weight percent, in water) suspension of carbon bundles, under the conditions where GA resulted in 50% dispersion of single carbon nanotubes.

To test the aggregation state of the tubes in the dispersion, X-ray scattering measurements of carbon tubes coated with GA were performed. The typical peaks which characterize the inter-tube packing within the ropes of as-produced SWNT disappeared in polymer-coated carbon tubes according to this invention (see Fig. 1). The microscopic structure of the stable dispersions was investigated using cryo-transmission electron microscopy (cryo-TEM). Cryo-TEM images show well separated single tubes, 2-3 nm in diameter (see Fig. 4). Such tubes can be clearly observed in suspensions both before and after drying and re-suspension. These observations demonstrated that adsorption of the GA leads to complete disruption of the inter-tube interactions in the crystalline ropes. Complementary evidences for the GA adsorption are given by FTIR measurements of the dried SWNT powder. The characteristic peaks due to carboxylate anion of the pure GA appear also in the dry SWNT powder (Fig. 5a).

Hence, the present invention relates to a method for the preparation of a dispersed aqueous suspension of carbon nanotubes, comprising adding to an aqueous medium, prior to the addition of carbon nanotubes or thereafter, a water-soluble polymeric material, thereby to separate the nanotubes into dispersed, essentially single tubes. Further, the present invention relates to a method for the preparation of dry non-tangled carbon nanotubes comprising dispersing nanotubes in an aqueous solution of a polymer as described above, and drying this dispersion.

25

The invention is also directed to the use of the carbon nanotubes in suspension or in powder in all applications where essentially single carbon tubes are required.

30 Based on the above findings, the present invention enables testing of single-tube properties, and comparisons to theoretical predictions. From the practical point of view, the ability to prepare a dry powder of single

tubes, well separated by a polymeric spacer, offers a by-pass to the tedious efforts involved in separating single tubes from an as-synthesized powder.

A possibility to prepare suspensions or powders of separated carbon nanotubes with defined properties, and controlled concentrations, enables to introduce the carbon nanotubes easily to any system, in any form and quantity, using known techniques for manipulating and portioning liquids and powders. This has direct applications in printing, coatings, thin layers, and molecular machines.

10

Since the polymer adsorbed on the carbon tubes acts as a compatibilizer, marked improvements can be achieved in the quality of the interface between nanotubes and the matrix. The long chain polymers, may serve as adhesion promoters leading to the formation of highly adhesive interfaces between the tubes and a polymeric matrix. It is well known that the typical adhesive fracture energy of a polymer-straightened interface is of the order of $10^2\text{-}10^3 \text{ J/m}^2$, about a 100 times higher than the fracture energy of a carbon-carbon plane. Thus, in one aspect, the invention also relates to the provision of a highly adhesive interface between carbon tubes and the polymeric matrix.

15

20

It is well known in material science that composite materials, comprising particles of one component homogeneously dispersed in a continuous phase, wherein the particle dimensions are in the order of nanometers, exhibit special mechanical properties. The main obstacle in producing these materials, called nanocomposites, is to overcome strong adhesive forces between the particles. The polymer coated carbon nanotubes according to the invention can be directly used in the production of nanocomposites, because of their excellent dispersion properties. Therefore, the invention further relates to the use of carbon nanotubes in the production of new composite materials. In one preferred embodiment,

25

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carbon nanotubes serve as an reinforcing agent in a polymer matrix. The preferred polymeric matrix in this embodiment is an elastomer.

It has been further shown that the suspensions of carbon nanotubes, prepared as described above, exhibit the presence of carbon nanotubes of 2-3 nm in diameter (Fig.4). The single-wall carbon nanotubes, as was described above, exhibit superb electrical properties. The invention is therefore also related to the deposition of nanotube powders or of droplets of nanotube dispersions at a relevant location in an electronic array,

where the tubes can serve as nanocontacts. The invention thus relates to the use of suspensions or powders of carbon nanotubes for creating an electric conductive connectors between two electronic devices, wherein one of the devices, or both of them, are nanoelectronic devices.

The present invention also relates to the use of a suspension or a powder of carbon nanotubes either for depositing carbon nanotubes onto a solid support in a required pattern, or as a template for the growth of crystals of silica or a hybrid material of silica with carbon nanotubes.

The present invention further relates to the use of a suspension or a powder of carbon nanotubes in a technique that comprises the formation of a thin layer. Said technique is preferably printing or coating.

The mechanism by which a polymer stabilizes the nanotube dispersions is based on the introduction of repulsive forces between adsorbed polymer chains. Both electrostatic and entropic repulsion, according to the composition of the mixture may play a role. Anyway, the introduction of a simple method for the preparation of polymer-coated tubes can remove a serious obstacle on the way to the mass production of ready-made nanotube-based additives, to be used in fields of printing, coatings, thin layers, molecular machines, reinforced elastomers and electronics.

Examples

Example 1

Gum arabic (Sigma) was dissolved in pure water to 15% (weight percent), and powder of as-produced nanotubes (from Carbolex, University of Kentucky, Lexington, Kentucky, USA) was added to 3 wt %. The mixture of 2 ml was then sonicated for 20 minutes. A homogeneous dispersion of SWNT was obtained. The suspension, that had an ink-like appearance, was stored at ambient temperature, and checked periodically for visual changes. The dispersion remained unchanged after four months, and the nanotubes did not settle when centrifuged at 4500 rpm for 30 minutes.

Example 2

10 ml of suspension, prepared as in Example 1, were evaporated in 20 ml flask yielding about 1.7 grams of fine black powder of polymer-coated SWNT. The powder was re-dispersed in 1.7 ml of pure water to obtain an ink-like homogeneous dispersion, which was stable.

Example 3

The following solutions were prepared: (A) 2 % GA , (B) 5 % GA, (C) 5 % SDS, (D) 15 % SDS, (E) 5 % CTAC, and (F) 15t% CTAC. Deionized water was used, SDS and GA were purchased from Sigma, CTAC from Aldrich. 10 ml of each solution were placed to a glass tube, 5 mg of polymer-coated SWNT, prepared as in example 2, were added to each tube, and the mixtures were sonicated. The tubes were then stored at ambient temperature and were visually checked for changes at intervals. In case of SDS and CTAC, their high concentration notwithstanding, a dark sediment appears within minutes to hours. Only in case of gum arabic, in both concentrations, the suspension was stable, as seen in Fig.3.

Example 4

Powder of as-produced nanotubes (from Carbolex) was characterized by X-ray scattering, using Philips x-ray powder diffractometer (PW-1050/70),

employed at 40kV/28mA with Cu K α (radiation wavelength $\lambda=0.154$ nm) radiation and graphite monochromator, the scattering vector being $q = 4\pi/\lambda \sin\theta$, θ being the scattering angle). Fig. 1a shows wide angle x-ray spectra of rope structure of a two-dimensional triangular lattice of SWNT with a lattice constant of 1.8 nm, and with evidence of multi-wall graphitic objects, which is in agreement with Thess et al. (P. Thess et al., Science 273 (1996) 483). Fig. 1b shows wide angle x-ray spectra of polymer-coated SWNT prepared as described in Example 2. The inset shows the reflections of the Co/Ni catalyst which is used in the synthesis of nanotubes. It can be seen that the inter-tube reflections, seen in Fig. 1a, disappear in Fig. 1b as a result of dispersing the rope structure to single individual carbon nanotubes. The two peaks, corresponding to graphite, may reflect presence of certain amounts of multiwall nanotubes in the as-prepared powder.

15

Example 5

The microscopic structure of the SWNT dispersions was investigated using cryo-transmission electron microscopy (cryo-TEM). The powder of Example 2 was re-dispersed in deionized water, 180 mg in 1 ml, and a drop of this dispersion was placed on a lacey TEM-grid on FORMVAR and vitrified in liquid ethane. The sample was imaged at -170°C using JEOL 1200EXII TEM equipped with a Gatan 626 coldstage which preserves the structure of the objects formed in the liquid phase. Fig. 4 presents a cryo-TEM image of the re-dispersed nanotubes. Well separated single tubes, 2-3 nm in diameter, are clearly observed (arrow with "S" in Fig. 4). Thicker, multiwall nanotubes can be also observed (arrow with "M").

25

Example 6

Powder of as-produced nanotubes (from Carbolex) was analyzed by Scanning Electron Microscope (JSM-35CF, JEOL, operated at 25kV). A micrograph of powder of Au-spattered, as-received nanotubes shows flexible ropes in randomly oriented networks. The arrow indicates a single rope.

30

Example 7

The powder of Example 2 was compared to GA by FTIR measurement. FTIR spectra of pellets, made with KBr, of pure GA (a), and the SWNT powder (b) were measured by Nicolet Protégé 460 spectrometer. Fig. 6
5 indicates that GA adsorbs to SWNT.

Modifications and variations of the present invention, as described above and illustrated in the examples, are possible. The invention can be applied
10 to the dispersal of carbon nanotubes, that were prepared by various procedures, wherein various suitable polymers can be used. The nanotubes may be used as a suspension or as a powder. The nanotubes may be used as an microelectronic element, as a template for crystal growth, as a component in composites, in printing, coatings, thin layers, molecular
15 machines, etc. It is therefore understood that within the scope of the appended claims, the invention may be realized otherwise than as specifically described.

CLAIMS

1. A method for the preparation of an aqueous suspension of carbon nanotubes, comprising adding to an aqueous medium, prior to the addition of carbon nanotubes or thereafter, a water-soluble polymeric material, thereby to separate the nanotubes into dispersed, essentially single tubes..
2. A method according to claim 1, wherein the polymer is a hydrophilic polymer, of either natural or synthetic origin.
3. A method for the preparation of dry non-tangled carbon nanotubes comprising: i) the preparation of an aqueous suspension of carbon nanotubes according to claim 1; and ii) the removal of water from said suspension.
4. A method of claim 3, wherein the removal of water comprises evaporation, lyophilization, or filtration.
5. A method according to any one of claims 1 to 4, wherein the concentration of dry, polymer-coated, carbon nanotubes in the suspension is up to 65% by weight.
6. A method according to any one of claims 1 to 5, wherein the mass ratio of polymer to carbon nanotubes ranges from 0.05 to 20.
7. A method according to any one of claims 1 to 6, wherein the polymer is chosen from polysaccharides and polypeptides.
8. A method according to any one of claims 1 to 6, wherein the polymer is a water soluble synthetic polymer.
9. A method according to any of claims 1 to 6, wherein the polymer comprises gum arabic, carrageenan, pectin, polygalacturonic acid, alginic acid, chitosan, and derivatives thereof

10. A method according to claim 8, wherein the polymer is a charged polymer.
11. A stable suspension of carbon nanotubes, prepared according to any one of claims 1 to 10.
12. A powder of carbon nanotubes, comprising a polymer in admixture therewith.
13. The powder of claim 12, wherein the polymer is adsorbed on the nanotubes.
14. Use of the carbon nanotubes of claim 11 or 12 for depositing carbon nanotubes onto a solid support in a required pattern.
15. Use of the carbon nanotubes of claim 11 or 12 as a template for the growth of crystals of silica, or a hybrid material of silica with carbon nanotubes.
16. Use of the carbon nanotubes of claim 11 or 12 as a reinforcing agent for polymeric matrices.
17. Use of the carbon nanotubes according to claim 16, wherein the polymeric matrix is elastomer.
18. Use of the carbon nanotubes of claim 11 or 12 as an electric conductive connector between two electronic devices.
19. Use according to claim 18, wherein one of the devices, or both of them, are nanoelectronic devices.
20. Use of the carbon nanotubes of claim 11 or 12 in a technique that comprises the formation of a thin layer.
21. Use according to claim 20, wherein the technique is printing.
22. Use according to claim 20, wherein the technique is coating.

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Loss of intertubular ordering in SWNT ropes

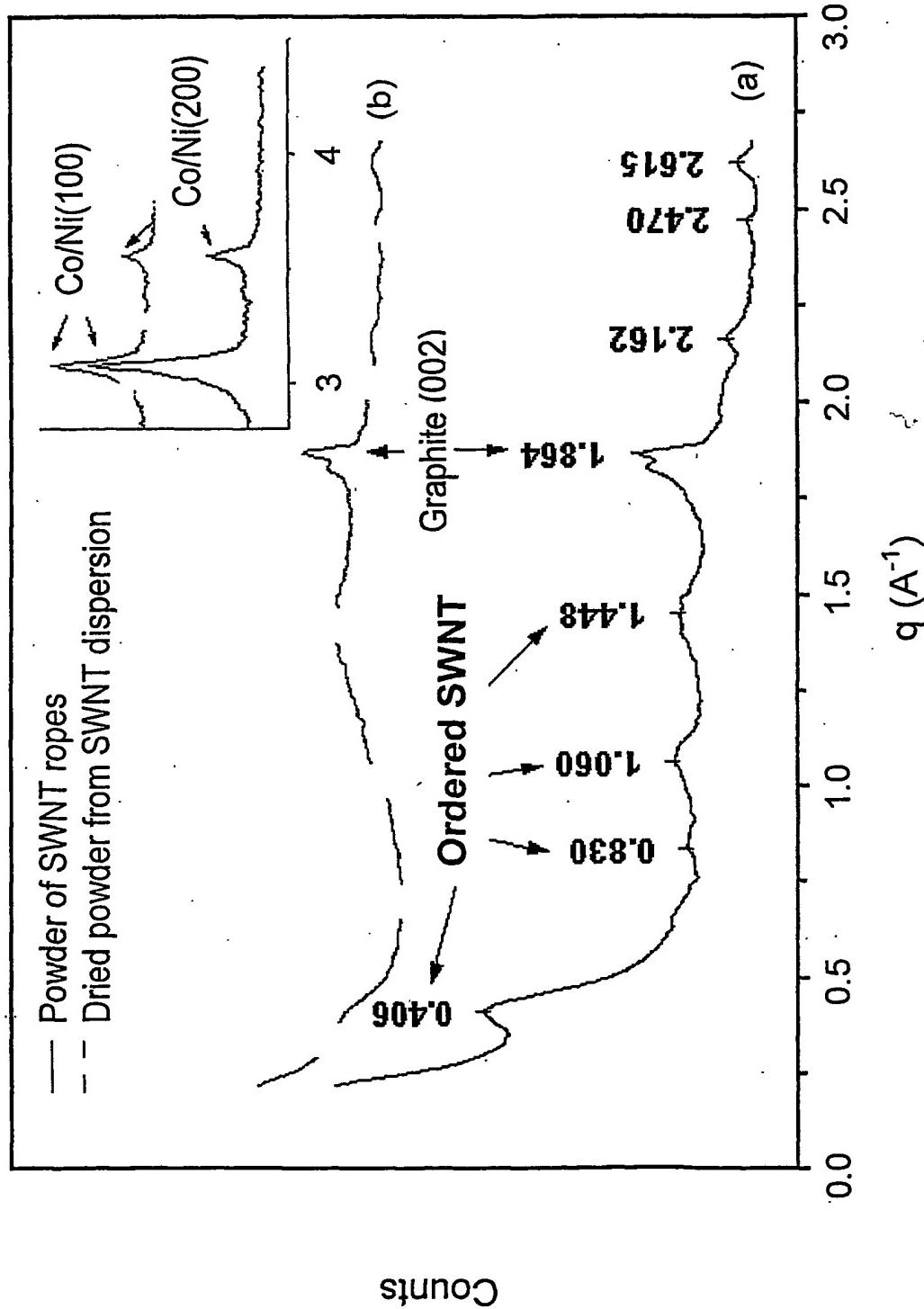


Fig. 1

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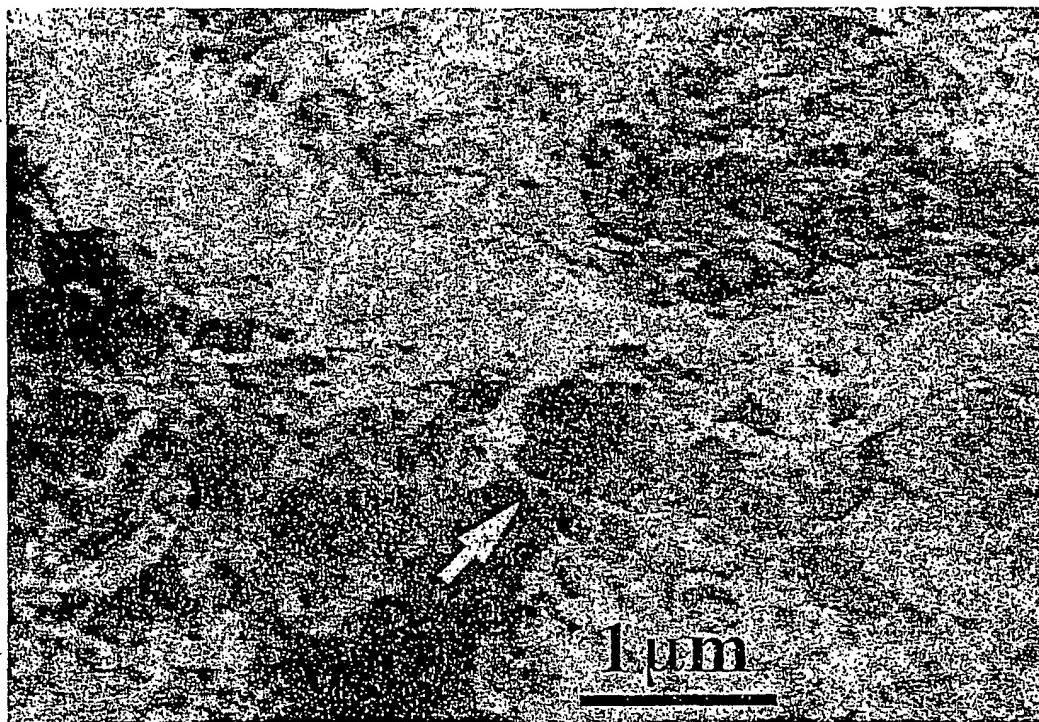


FIG. 2
Irreducible Copy

Fig. 2

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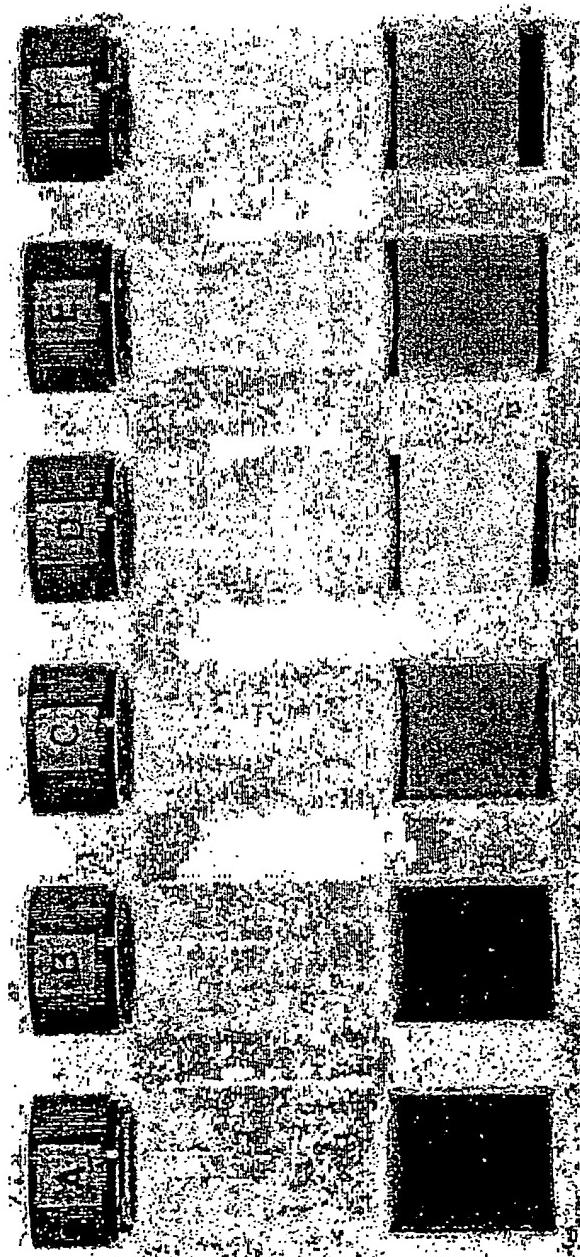
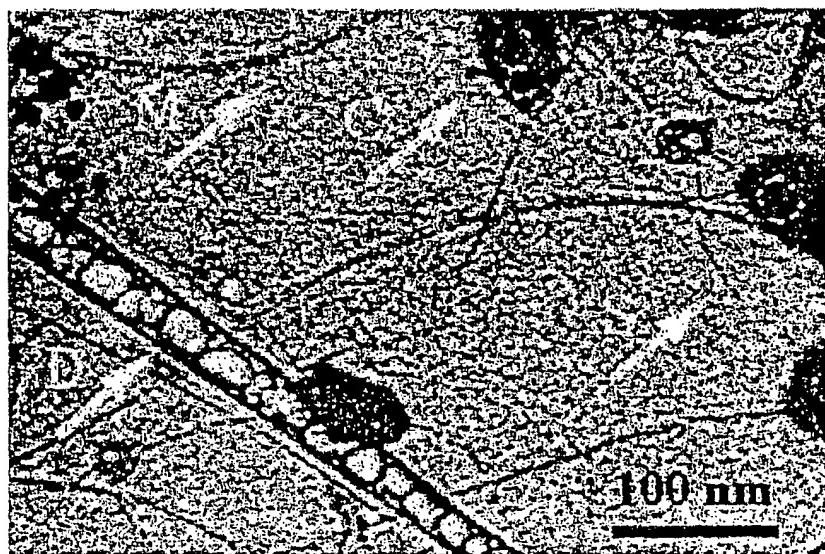


Fig. 3

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Fig. 4

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Dried SWNT powder showing adsorbed gum arabic

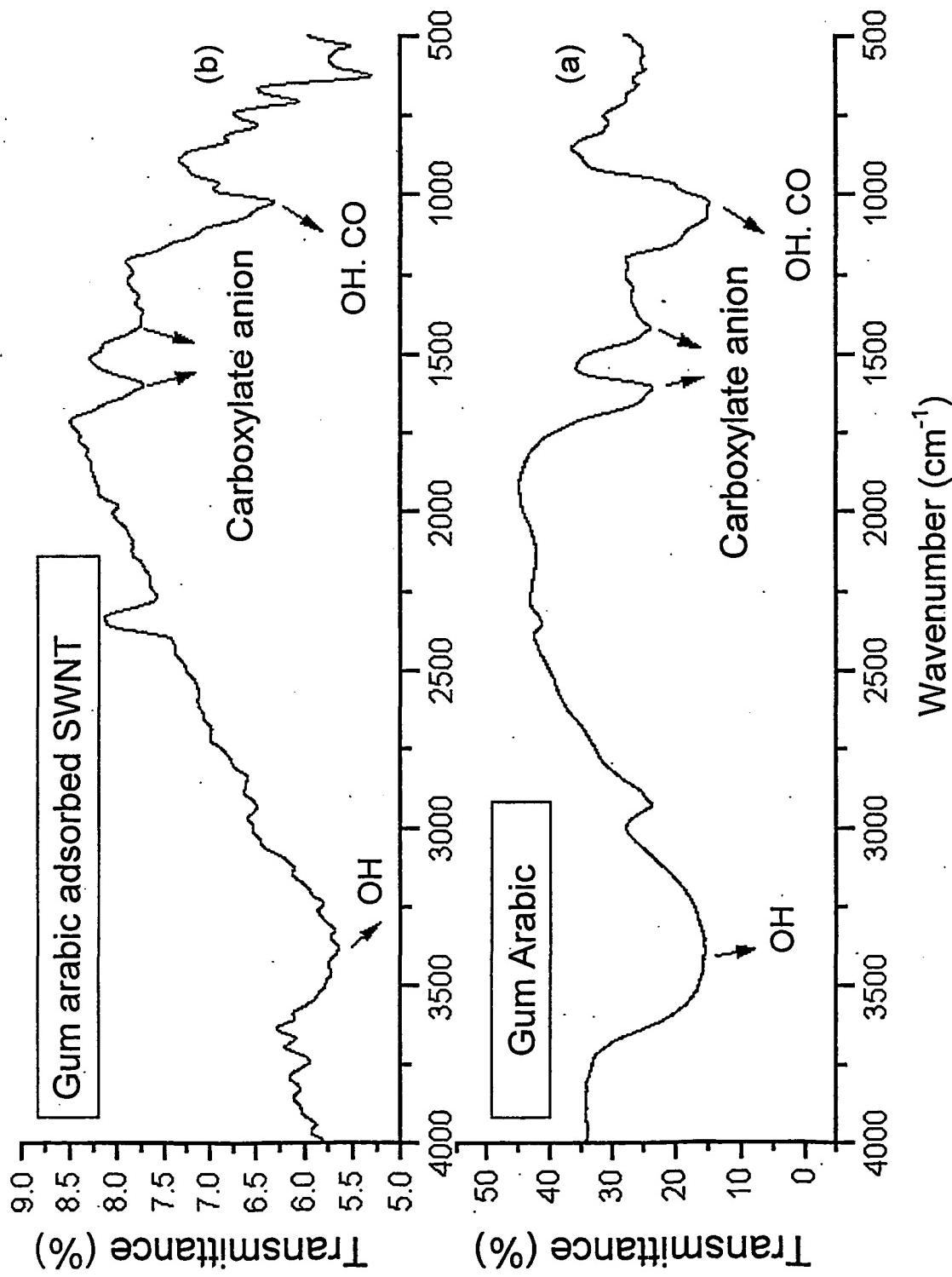


Fig. 5

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B31/02 C08K7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P, X	<p>O'CONNELL M J ET AL: "Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping" <i>CHEMICAL PHYSICS LETTERS</i>, vol. 342, no. 3-4, 13 July 2001 (2001-07-13), pages 265-271, XP002207175 ISSN: 0009-2614 the whole document</p> <p>---</p> <p>-/-</p>	1, 2, 12, 13

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHAFFER M S P ET AL: "Fabrication and characterization of carbon nanotube/poly(vinyl alcohol) composites" ADVANCED MATERIALS, 3 AUG. 1999, VCH VERLAGSGESELLSCHAFT, GERMANY, vol. 11, no. 11, pages 937-941, XP002206256 ISSN: 0935-9648 page 938, left-hand column page 940, right-hand column ---	1,2,8, 11-13, 16,20
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>SHAFFER M S P ET AL: "Dispersion and packing of carbon nanotubes" CARBON, vol. 36, no. 11, 1998, pages 1603-1612, XP002206259 ISSN: 0008-6223 page 1604, right-hand column -page 1605, left-hand column -----</p> <p>AUSMAN K D ET AL: "Organic solvent dispersions of single-walled carbon nanotubes: toward solutions of pristine nanotubes" JOURNAL OF PHYSICAL CHEMISTRY B, vol. 104, no. 38, 28 September 2000 (2000-09-28), pages 8911-8915, XP002206260 ISSN: 1089-5647 -----</p>	1,2,11, 20